Energy dependent saturation width of swift heavy ion shaped embedded Au nanoparticles

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The transformation of Au nanoparticles (NPs) embedded in SiO_2 from spherical to rod-like shapes induced by swift heavy ion irradiation has been studied. Irradiation was performed with ^{197}Au ions at energies between 54 and 185 MeV. Transmission electron microscopy and small angle x-ray scattering measurements reveal an energy dependent saturation width of the NP rods as well as a minimum size required for the NPs to elongate. The NP saturation width is correlated with the ion track diameter in the SiO_2. NP melting and in-plane strain in the irradiated SiO_2 are discussed as potential mechanisms for the observed deformation. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3099971]

Embedded metal nanoparticles (NPs) have received considerable attention due to their high potential for application in optical filters, memories, or switching devices. Crucial parameters determining the optical properties of NP composite materials include the NP composition, size, shape, and orientation. The surface plasmon resonance, for example, which governs the optical absorption properties of metal NPs, is critically dependent on the NP shape with a split in the resonance band for rod-shaped particles due to transverse and longitudinal modes of the charge density oscillations.[1] The development of protocols to form embedded NPs with application-specific size, shape, and orientation is thus a prerequisite for effective device fabrication. Recently, a process by which spherical metal NPs embedded in SiO_2 are deformed to rod-like shapes under swift heavy ion (SHI) irradiation was investigated for Co,[2] Au,[3–5] Ag,[6] and Pt (Ref. 7) NPs. For all elements, the direction of elongation was parallel to the incident ion beam. Experiments with Au NPs demonstrated a minimum electronic energy deposition, comparable to that required to form a molten ion track in amorphous SiO_2, was necessary for NP elongation. Furthermore, the intrinsic role of the SiO_2 matrix in the process was established given no deformation was observed for free standing Au NPs under SHI irradiation.[4] Though a definitive theory for the deformation process has yet to be established, suggestions for potential mechanisms involved include melting of the NPs in a thermal spike,[2,8] creep deformation induced by an overpressure due to differences in volume expansion and compressibility of NP and matrix material,[2] and stress-driven deformation due to irradiation induced in-plane strain perpendicular to the ion beam direction.[4] In this work we demonstrate a clear correlation between the dimensions of the deformed NPs and the molten ion track in the SiO_2 induced by the SHI irradiation. This represents not only a step forward in understanding the deformation process but also demonstrates a means of controlled tuning of the NP dimensions.

For NP synthesis, we implanted 1.2 MeV ^{197}Au ions with a total fluence of 1×10^{17} ions/cm^2 into ~2 μm thick SiO_2. The SiO_2 was thermally grown on Si (100) substrates. Implantation was carried out at room temperature. The samples were then annealed in O_2 at 1100 °C for 3 h in a conventional quartz tube furnace where O_2 enhances the growth of Au NPs.[9] The NPs were irradiated with ^{197}Au ions at 54, 89, and 185 MeV at the ANU Heavy Ion Accelerator Facility with average energy losses over the depth of the SiO_2 layer of 7.5, 11.0, and 16.5 keV/nm, respectively, as estimated by SRIM 2006 calculations.[10] At these energies, nuclear stopping is negligible and the energy loss is thus virtually only due to electronic stopping. Fluences ranged between 6.6×10^{12} and 6.6×10^{14} ions/cm^2.

The NPs were characterized using transmission electron microscopy (TEM) and synchrotron small angle x-ray scattering (SAXS) in transmission geometry. SAXS provides an efficient way to quantify the elongation process, rapidly sampling a large number of particles and thus yielding vastly improved statistics compared to TEM analysis. The SAXS measurements were performed at the ChemMatCARS beamline 15ID-D of the Advanced Photon Source, Argonne National Laboratories, USA, using an x-ray wavelength of 1.1 Å (~11.27 keV) and camera lengths of 555, 1894, and 6880 mm. Samples were prepared by locally removing the Si substrate to isolate the thin SiO_2 film containing the NPs.[11] This enables measurements of the thin film only and negates artifacts due to diffraction from the single crystalline substrate and scattering from irradiation induced inhomogeneities therein. SAXS measurements were performed with the incident x rays aligned normal to the sample surface (or equivalently parallel to the nanorods). At this geometry, the isotropic SAXS images represent the evolution of the NP width. Measurements with the samples tilted off-axis (not shown here) confirmed the shape anisotropy. Scattering from SiO_2 without embedded NPs was measured for background re-

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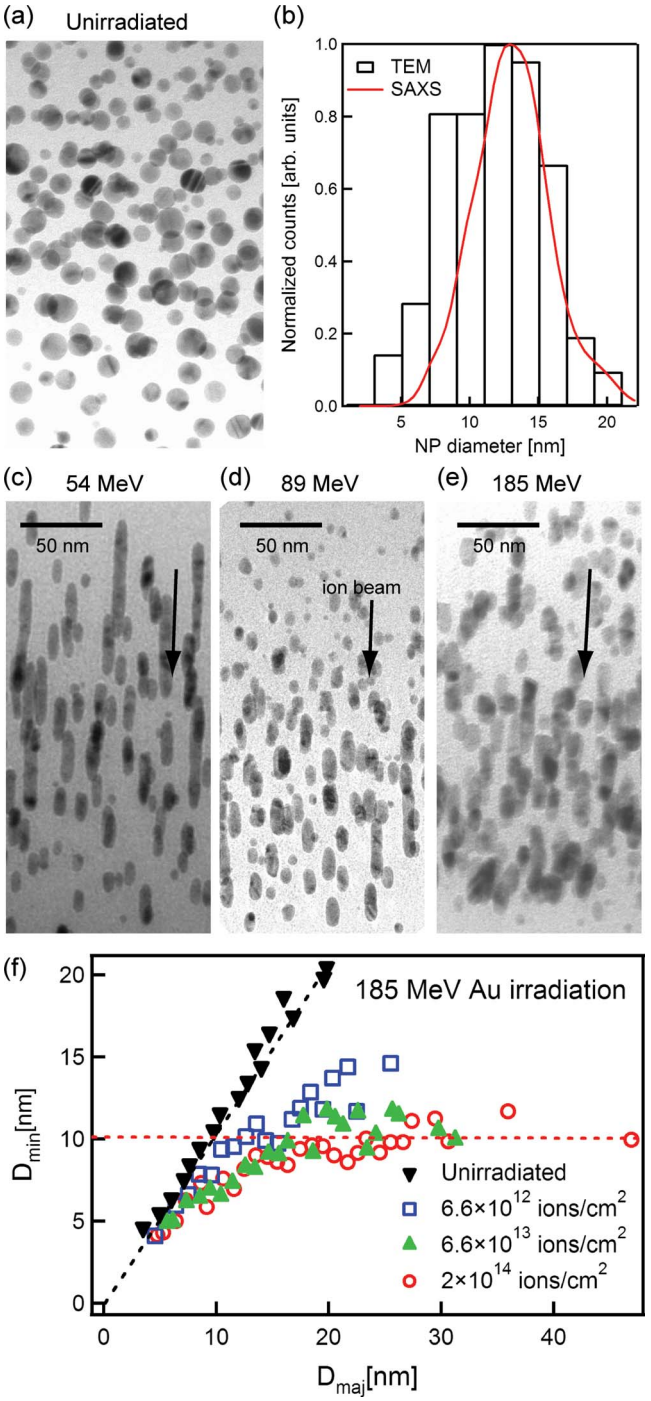

FIG. 1. (Color online) Cross-section TEM images of (a) unirradiated Au NPs, and Au NPs irradiated with 2×10^{14} ions/cm^2 Au ions at (c) 54 MeV, (d) 89 MeV, and (e) 185 MeV. The arrows indicate the direction of the incident ion beam. (b) Size distribution of the unirradiated NPs extracted from TEM and SAXS measurements. (f) NP width (D_{min}) as a function of NP length (D_{maj}) for Au NPs irradiated at 185 MeV.

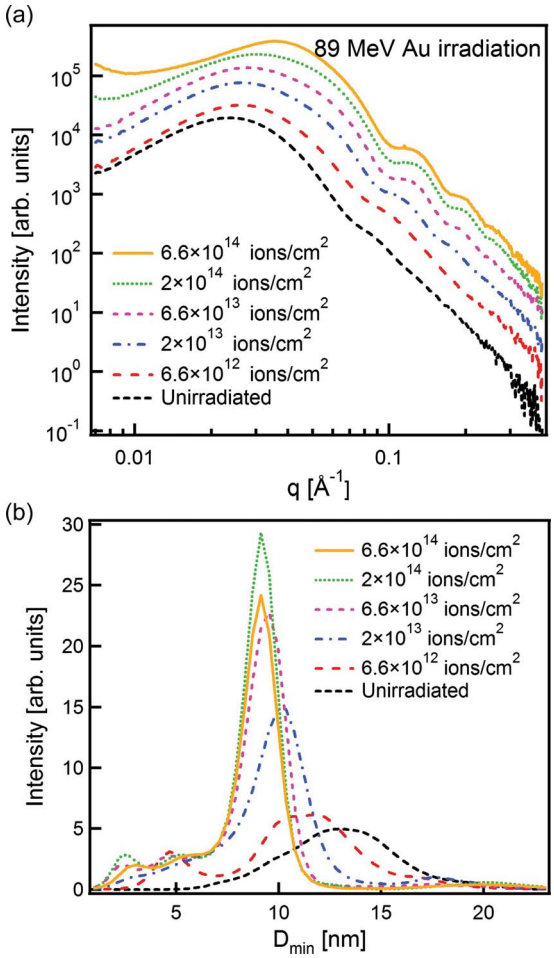

FIG. 2. (Color online) (a) SAXS spectra of Au NPs irradiated at 89 MeV and (b) corresponding distributions of the NP width D_{min} for a series of ion fluences.

moval. Quantitative analysis was performed using a maximum-entropy method.[7,12]

The cross-sectional TEM images in Fig. 1 show the Au NPs (a) prior to irradiation and after irradiation at energies of (c) 54 MeV, (d) 89 MeV, and (e) 185 MeV at a fluence of 2×10^{14} ions/cm^2. Before irradiation, the NPs are spherical in shape with a broad distribution of sizes and an average diameter of ~12 nm [see Fig. 1(b)]. Upon SHI irradiation, the Au NPs elongate to form nanorods in the direction of the ion beam as consistent with previous investigations. From the images in Figs. 1(c)–1(e), it is apparent that the given fluences are sufficient to transform the spherical NPs into nanorods with uniform widths and a broad distribution of aspect ratio. The nanorod width is clearly dependent on the irradiation energy. For quantitative analysis, we have plotted in Fig. 1(f) the NP width (defined as the minor axis D_{min} of the deformed NP) as a function of the NP length (defined as the major axis D_{maj} of the deformed NP) extracted from TEM images for a series of fluences at 185 MeV irradiation. Not all NPs are elongated; those with diameter 7 nm or less remain spherical, while larger NPs progressively change shape into nanorods with aspect ratio as high as five. The NP width saturates at a value just above 10 nm as indicated by the dashed line. Figure 2 shows an example of SAXS measurements of the Au NPs irradiated at 89 MeV for a series of fluences. The presence of oscillations in the scattering intensity in Fig. 2(a) at high irradiation fluences is indicative of a narrow distribution of NP widths. The corresponding distributions of NP widths D_{min} are shown in Fig. 2(b). Clearly the initially wide distribution narrows and the mean value decreases with increasing irradiation fluence. Above a fluence of 2×10^{14} ions/cm^2, no further change in the mean NP width was observed indicating saturation. A decrease in intensity is apparent, consistent with NP dissolution. A similar trend was apparent for all irradiation energies. The saturation NP width D_{min}^{sat} extracted from SAXS measurements is plotted in Fig. 3 as a function of the electronic stopping power in

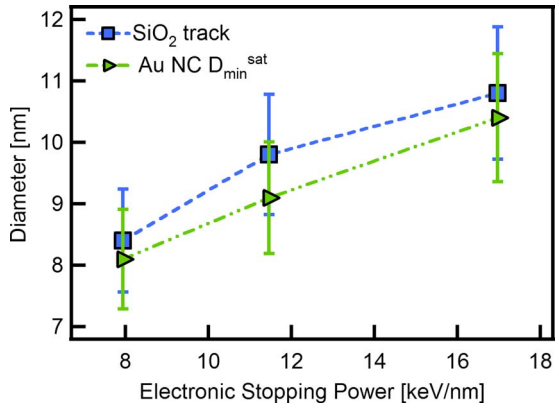

FIG. 3. (Color online) Saturation width of the irradiated Au NPs D_{min}^{sat} and ion track diameter (see Ref. 13) as a function of electronic stopping power in SiO_2.

SiO_2 along with the ion track diameter in amorphous SiO_2 for identical irradiation conditions.[13]

The energy dependent saturation of the NP width is potentially the result of local melting of both the SiO_2 and NPs in a thermal spike in combination with in-plane strain. The latter leads to the ion hammering effect, responsible for the plastic deformation of the SiO_2 as the ion passes through the material as illustrated by the deformation of freestanding SiO_2 spheres under SHI irradiation.[14] In contrast to the Au NPs, these spheres elongate perpendicular to the incident ion beam direction. It was suggested that the in-plane strain in the SiO_2 matrix compresses the Au NPs leading to their elongation along the ion beam direction.[4] The lack of NP elongation in the absence of a sufficiently thick (or any) surrounding matrix supports this theory.[5] However, the calculations of Klaumünzer[15] using a viscoelastic model show that the generated strain is most likely insufficient to deform the NPs and thus the NPs must play an active role in the deformation process. Furthermore this mechanism cannot explain the observed energy dependence of the saturation of the NP width. Estimates by Awazu *et al.*[8] using a thermal spike model indicate that Au NPs below 20 nm melt under SHI irradiation with stopping powers of approximately 29 and 9 keV/nm in Au and SiO_2, respectively. We suggest that the deformation results from a combination of in-plane strain and NP melting. Upon NP melting, elongation is potentially a means of relaxing in-plane strain. The elongation is confined by the molten ion track as apparent from Fig. 3, which demonstrates a clear correlation between NP saturation width D_{min}^{sat} and ion track diameter. NPs smaller than the ion track do not deform or deform at a significantly lesser rate given they are already effectively confined.

In conclusion, an energy dependent saturation width for Au NPs elongated by SHI irradiation has been demonstrated. The NP saturation width is directly correlated with the ion track diameter in SiO_2. The elongation mechanism is consistent with deformation of the molten NP confined to the molten ion track as a consequence of irradiation induced in-plain strain in the SiO_2. This process readily enables tailoring of the NP dimensions to application-specific requirements.

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